

Introduction and Application of the Activity Concept in the Chemistry of Fused Salts and Slags*

K. GRJOTHEIM, C. KROHN

*Institute of Inorganic Chemistry, The Technical University of Norway,
Trondheim*

Using the Temkin definition of activities in molten salts, a method for the calculation of the thermodynamic activity in molten reciprocal salt mixtures is discussed. The method is based on classical thermodynamics, viz: the metathetical reactions in the system, the measured ionic exchange equilibria and the Gibbs—Duhem equation.

I. Introduction

The activities of the respective components in a mixture of fused salts or slags is of primary interest in theoretical metallurgy. Equilibrium calculations in metallurgy involve the application of the mass action law, but this presupposes knowledge of how the activities of the reacting components vary with the composition of the mixture.

The present paper will briefly review how the activity concept is introduced in thermodynamics, and give some examples of its application in fused salts. Thus, a method for calculating the activities in reciprocal salt systems from experimental data is briefly sketched.

II. The activity concept

Although activity originally was defined as relative fugacity (Lewis, 1908), the transition from chemical potential to activity is now best done in connection with the following equation:

$$\mu_{MA} - \mu_{MA}^0 = RT \ln a_{MA} - RT \ln a_{MA}^0, \quad (1)$$

where μ_{MA} and μ_{MA}^0 are the chemical potentials of the two different states and a_{MA} and a_{MA}^0 are the corresponding activities of MA. It is customary to attribute a specific value to μ_{MA}^0 , namely, the chemical potential in an arbitrarily selected standard system where we set *the activity of MA equal to unity by definition*.

Applying the mass action law to the chemical equilibrium:

$$\sum_{i=1}^i \nu_{A_i} A_i = \sum_{j=1}^j \nu_{B_j} B_j, \quad (2)$$

* Presented at the 1st Czechoslovak Symposium on the Problems of Aluminium-Production in Smolenice, ČSSR, June 7—9, 1966.

we get:

$$K = \frac{\prod_{j=1}^j a_{B_j} \nu_{B_j}}{\prod_{i=1}^i a_{A_i} \nu_{A_i}} \quad \text{eq} \quad (3)$$

where K is a constant independent of the concentrations in the equilibrium state. For an ideal mixture we can introduce the mole fractions instead of the activities in the equilibrium state. For the non-ideal solution mole fractions again may be introduced, but in this case also a *concentration dependent* expression containing the activity coefficients must be introduced.

In thermodynamics the following relation between the relative partial molar quantities is valid (for a component in its standard state being transferred to a mixture):

$$\Delta \bar{G}_i = \Delta \bar{H}_i - T \Delta \bar{S}_i. \quad (4)$$

Since the chemical potential and the partial molar Gibbs' free energy is the same, the activities can be expressed as follows:

$$\Delta \bar{G}_i = \Delta \mu_i = RT \ln a_i = \Delta \bar{H}_i - T \Delta \bar{S}_i. \quad (5)$$

The relative partial molar enthalpy is a measure of the difference in bonding energy for one mole of the component in the mixture and in the pure state. Correspondingly, the relative partial molar entropy represents the degree of disorder in the mixture as compared to that of the pure state (when assuming that the non-configurational contribution to the entropy is negligible).

The expression for the activity thus contains two entirely different terms that express deviations from ideality. Although $\Delta \bar{S}_i$ formally depends on $\Delta \bar{H}_i$:

$$\left(\frac{\partial H}{\partial T} \right)_p = C_p = T \left(\frac{\partial S}{\partial T} \right)_p.$$

Many non-ideal mixtures have sufficient thermal energy to neutralize the tendency to non-statistical distribution due to the difference in bonding forces. Mixtures of this type will therefore have approximately ideal entropy of mixing. J. Hildebrand [1] has introduced the term *regular solutions* for such mixtures, where then $\Delta \bar{H}_{MA}^{\text{reg}} \neq 0$ and $\Delta \bar{S}_{MA}^{\text{reg}} = \Delta \bar{S}_{MA}^{\text{ideal}}$.

For an ideal solution, thermodynamics require that

$$\Delta \bar{H}_{MA} = 0 \quad \text{and} \quad \Delta \bar{S}_{MA}^{\text{ideal}} = -R \ln N_{MA}.$$

Hence it appears that the choice of concentration measure is decisive for

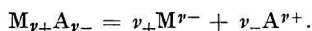
what we shall understand as the ideal solution. From classical thermodynamics it appears that the most convenient choice of concentration measure is based on a knowledge of the structure of the mixtures under consideration (compare with aqueous solutions or gas mixtures).

III. Definition of an ideal salt melt

The basis of a thermodynamic treatment of activities in molten salts is based on the conception of salt melts being built up of ions. This is in accordance with the accepted view on the structure of inorganic solids. These are for a substantial part assumed to consist of electrically charged ions, where each ion is surrounded by a certain number of ions of opposite charge. The electroneutrality requirement is met by a reciprocal action between several ions of opposite charge without referring to specific molecules. Because of the coulombian repulsion between ions of the same charge and the reciprocal attraction between positive and negative ions, we get a certain local ordering in molten salts corresponding to that in the solid salt. However, while a long-range order appears in the crystal, disorder prevails in the melt over longer distances.

One consequence of this evaluation of experimental facts will be that the activity of a salt in a salt solution is most conveniently expressed by the concentration of the ions going into the salt. In classical thermodynamics, the activities appearing in the mass action law will always refer to neutral materials, i. e., atoms, molecules or ion pairs.

As an example where ion pairs are involved, we shall consider a salt dissociating into ions according to the following scheme:



We can apply the thermodynamic mass action law, regardless of the degree of dissociation:

$$K = \frac{a_+^{\nu_+} \cdot a_-^{\nu_-}}{a_{MA}}. \quad (6)$$

Since the constant K is unknown when the degree of dissociation is unknown, we standardize the salt activity so that $K = 1$, i. e. the relation between the salt activity and ion activity is *by convention* the following:

$$a_{MA} = a_+^{\nu_+} \cdot a_-^{\nu_-}. \quad (7)$$

We thus can, if it is desirable, introduce as the concentration measure the ionic product and activity coefficients as we use them in the treatment of electrolytic aqueous solutions.

H. Temkin's analogous definition [2] of an ideal salt solution is based in

the statistical equality in an „ideal salt melt“ of *all* ions with the *same* sign of electric charge, regardless of the magnitude of the charge or the relative ion sizes. Consequently, one can look upon an ideal ionic solution as consisting of the two mutually independent cation and anion solutions. Then the integral entropy of mixing for molten salts will consist of one cation and one anion contribution. A salt melt consisting of n_{Na} moles of Na^+ , n_{K} moles of K^+ , n_{Cl} moles of Cl^- and n_{Br} moles of Br^- ions, respectively, will, according to Temkin, have an ideal entropy of mixing equal to:

$$\Delta S^{\text{ideal}} = -R(n_{\text{Na}} \ln N_{\text{Na}} + n_{\text{K}} \ln N_{\text{K}} + n_{\text{Cl}} \ln N_{\text{Cl}} + n_{\text{Br}} \ln N_{\text{Br}}) \quad (8)$$

where the concentration measure N represents ionic fractions:

$$N_{\text{Na}} = \frac{n_{\text{Na}}}{n_{\text{Na}} + n_{\text{K}}}, \text{ etc.} \quad (9)$$

According to equation (5), the ideal partial molar entropy of a component in the solution will be:

$$\Delta \bar{S}_{\text{NaCl}}^{\text{ideal}} = -R \ln (N_{\text{Na}} N_{\text{Cl}}). \quad (10)$$

Taking into account that for the ideal mixture $\Delta \bar{H}_{\text{NaCl}} = 0$, the activity of the component in the ideal salt melt may be expressed by

$$a_{\text{NaCl}}^{\text{ideal}} = N_{\text{Na}} N_{\text{Cl}}. \quad (11)$$

For a non-ideal salt melt, one introduces the activity coefficients:

$$a_{\text{NaCl}} = N_{\text{Na}} N_{\text{Cl}} \gamma_{\text{NaCl}}. \quad (12)$$

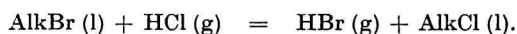
Temkin's definition of an ideal ionic solution is, as can be seen, very simple, and experimental results have demonstrated its applicability in approximate calculations.

IV. Experimental results

A. Mixtures of salts with a common ion

The simplest ionic mixtures from a structural point of view are the alkali halides. Since the ionic constituents of these salts have noble gas electron configurations, it must be expected that theories based on simple ion models will best fit the experimental data. There was, up to some years ago, except for phase diagrams, a lack of experimental thermodynamic data available for these systems. Within the experimental and computational limits of accuracy for the cryoscopic data, these melts can mainly be considered as ideal according to Temkin's definition.

During the last few years, H. Flood et al. [3] have studied ion exchange equilibria of the following type:



From these equilibrium data and recent, very accurate calorimetric heat of mixing data

for these binary mixtures (O. J. Kleppa et al. [4]), one may calculate activities in these systems.

Melts of this sort may exhibit both positive and negative deviation from ideality. For the binary alkali halide systems with a common cation, the deviation is very small. The accurate value of the deviation from ideal solution is most interesting from a theoretical point of view.

To the practical metallurgist it is satisfactory to know that the activities in these melts can be calculated on the basis of ideal ion models, or for melts with 18 shell ions like silver, as regular solutions.

The anions are usually the larger ions of a molten salt, and it is reasonable to expect that the anions of a mixture may be distributed at random, even when the number of charges on the anions is different. In the case of a wide difference in field strength of the cations in an ionic mixture, extremely large deviations from random ionic mixing may occur. In this case, the mixture may more conveniently be regarded as consisting of new, complex, ionic species.

B. Reciprocal salt pairs

From classical thermodynamics and expression for the activity coefficients in melts of reciprocal salt pairs is derived in the following, and the necessary experimental data to put the formulae to use, are discussed.

We will consider as an example a melt consisting of the ions: Na^+ , K^+ , Cl^- and Br^- . Because of the electroneutrality restriction:

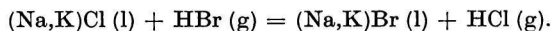
$$n_{\text{Na}} + n_{\text{K}} = n_{\text{Cl}} + n_{\text{Br}} \quad (13)$$

this system will have only three independent constituents. For the mathematical treatment, it is more convenient to consider the system as consisting of the four components NaCl , NaBr , KCl and KBr , respectively, with the corresponding activity coefficients. To derive these, four independent thermodynamic equations are imperative.

The first equation to combine the unknown activity coefficients is the Gibbs—Duhem equation, which by the introduction of ionic fractions takes on the following form:

$$N_{\text{Cl}} \ln \gamma_{\text{NaCl}} + (N_{\text{Na}} - N_{\text{Cl}}) \ln \gamma_{\text{NaBr}} + N_{\text{K}} \ln \gamma_{\text{KBr}} = 0. \quad (14)$$

Next, the anion exchange reaction may be considered. This can be written:



The thermodynamic equilibrium constant for this reaction, in terms of Temkin's activity expressions, will be:

$$K_{\text{mix}} = \frac{N_{\text{Br}} p_{\text{HCl}}}{N_{\text{Cl}} p_{\text{HBr}}} \cdot \underbrace{\left(\frac{\gamma_{\text{NaBr}}}{\gamma_{\text{NaCl}}} \right)}_{K_{\text{mix}}^{\text{an}}} N_{\text{Na}} \cdot \left(\frac{\gamma_{\text{KBr}}}{\gamma_{\text{KCl}}} \right) N_{\text{K}}. \quad (15)$$

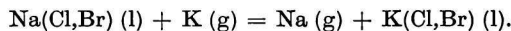
$K_{\text{mix}}^{\text{an}}$ is the denotation for the „ideal equilibrium constant“ for the anion exchange. Introducing the change in standard Gibbs' free energy for the same anion exchange in pure sodium-, ΔG_{Na}^0 , respectively pure potassium environment, ΔG_{K}^0 , into (15) gives the following equation:

$$\varphi_2 = \ln K_{\text{mix}}^{\text{an}} = -\frac{1}{RT} (N_{\text{Na}} \Delta G_{\text{Na}}^0 + N_{\text{K}} \Delta G_{\text{K}}^0) - N_{\text{Na}} \ln \left(\frac{\gamma_{\text{NaBr}}}{\gamma_{\text{NaCl}}} \right) - N_{\text{K}} \ln \left(\frac{\gamma_{\text{KBr}}}{\gamma_{\text{KCl}}} \right). \quad (16)$$

Exchange equilibria of this type were introduced by H. Flood and A. Muan [5], and they have proved to be very useful for thermodynamic equilibrium calculations in molten salts and slags.

In the equation (16) the respective ionic fractions, vapour pressures and activity coefficients refer to the equilibrium mixture in the reciprocal system. This equation gives the apparent equilibrium constant as a function of the cation concentration in the mixture. This function can be determined experimentally.

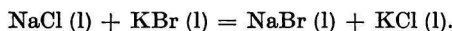
A third equation is in an analogous manner obtained by considering the cation exchange equilibria in the equilibrium mixture:



Since the procedure is identical with the one already given, only the result will be presented:

$$\begin{aligned} \varphi_1 = \ln K_{\text{mix}}^{\text{cat}} = \ln \left(\frac{N_{\text{K}} p_{\text{Na}}}{N_{\text{Na}} p_{\text{K}}} \right) &= \frac{1}{RT} (N_{\text{Cl}} \Delta G_{\text{Cl}}^0 + N_{\text{Br}} \Delta G_{\text{Br}}^0) - N_{\text{Cl}} \ln \left(\frac{\gamma_{\text{KCl}}}{\gamma_{\text{NaCl}}} \right) - \\ &- N_{\text{Br}} \ln \left(\frac{\gamma_{\text{KBr}}}{\gamma_{\text{NaBr}}} \right). \end{aligned} \quad (17)$$

A fourth equation may be derived from a consideration of the reciprocal equilibrium in the system



Introduction of Temkin's activity expressions in the equilibrium constant for this reaction gives the equation:

$$\ln \gamma_{\text{NaCl}} + \ln \gamma_{\text{KBr}} - \ln \gamma_{\text{NaBr}} - \ln \gamma_{\text{KCl}} = -\frac{\Delta G_{\text{ex}}^0}{RT}, \quad (18)$$

where ΔG_{ex}^0 can be taken from thermodynamic tables.

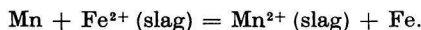
From these four equations expressions for the activity coefficients are derived. For γ_{NaCl} we get the following at an arbitrary concentration (N_{Na}^* , N_{Cl}^*):

$$\begin{aligned} \ln \gamma_{\text{NaCl}} &= (1 - N_{\text{Na}}^*) \cdot \varphi_1(N_{\text{Na}}^*, 0) - \int_1^{N_{\text{Na}}^*} \varphi_1(N_{\text{Na}}, 0) dN_{\text{Na}} + \\ &+ (1 - N_{\text{Na}}^*) \int_1^{N_{\text{Cl}}^*} \left[\frac{\partial \varphi_2(N_{\text{Na}}^*, N_{\text{Cl}})}{\partial N_{\text{Na}}} \right]_{N_{\text{Cl}}} dN_{\text{Cl}} + \\ &+ (1 - N_{\text{Cl}}^*) \varphi_2(N_{\text{Na}}^*, N_{\text{Cl}}^*) - \int_1^{N_{\text{Cl}}^*} \varphi_2(N_{\text{Na}}^*, N_{\text{Cl}}) dN_{\text{Cl}}. \end{aligned} \quad (19)$$

Analogous expressions are obtained for the other activity coefficients. As can be seen from this formula, it is possible to calculate the activity coefficient for sodium chloride, γ_{NaCl} , for any given concentration (N_{Na}^* , N_{Cl}^*) in the system, provided the anion exchange function, φ_2 , is known over the whole concentration range in the reciprocal mixture, and the cation exchange function, φ_1 , is known only for the binary system NaCl—KCl.

H. Flood et al. [3] have, as previously mentioned, studied a number of bromine-chlorine exchange reactions in the alkali halides. Cation exchange equilibria, however, are very difficult to study experimentally, and reliable data for the system NaCl—KCl are at present not available. It is possible, by using thermodynamic equations, to modify further the equation for γ_{NaCl} into expressions containing the activity coefficients of NaCl and KCl in the binary systems instead of the cation exchange function. By introducing experimental values into these modified equations together with Flood et al.'s data for the chlorine-bromine exchange, it has been possible to calculate γ_{NaCl} . The preliminary results must be expected to be only semi-quantitative, because the derived formula is very sensitive to inaccuracy in the exchange equilibrium constants close to the integration limits. In addition, the applied activity data for the system NaCl—KCl are uncertain. We are, however, working to improve both conditions.

The equations for the exchange equilibria have proved to be very useful in thermodynamic calculations of a number of metallurgical equilibria. Many of these reactions may be considered as cation exchanges in mixed anion environment and anion exchanges in mixed cation environment, respectively. As an example we can take the manganese distribution between the steel bath and a basic slag. This reaction can be formulated as a cation exchange according to the scheme:



The equilibrium constant for this reaction should depend on the anions present, and in a simple basic slag containing only the anions O^{2-} and SiO_4^{4-} , the relation between the equilibrium constant and the composition ought to be as follows:

$$\log K = N'_{\text{O}^{2-}} \cdot \log K_{\text{O}} + N'_{\text{SiO}_4^{4-}} \cdot \log K_{\text{SiO}_4}. \quad (20)$$

The parameters $N'_{\text{O}^{2-}}$ and $N'_{\text{SiO}_4^{4-}}$, respectively, are the *equivalent* ionic fractions, defined as:

$$\begin{aligned} N'_{\text{O}^{2-}} &= \frac{2n_{\text{O}^{2-}}}{2n_{\text{O}^{2-}} + 4n_{\text{SiO}_4^{4-}}}, \\ N'_{\text{SiO}_4^{4-}} &= \frac{4n_{\text{SiO}_4^{4-}}}{2n_{\text{O}^{2-}} + 4n_{\text{SiO}_4^{4-}}}. \end{aligned} \quad (21)$$

Provided we have ideal ionic melts, or activity coefficients that mutually compensate, we can set the equilibrium constant equal to:

$$K = \frac{N_{\text{Mn}^{2+}}}{N_{\text{Fe}^{2+}} \cdot [\text{Mn}] (\text{in Fe})}. \quad (22)$$

K_{O} and K_{SiO_4} , respectively, represent the distribution equilibrium constant in pure oxide and pure silicate environment. As has been shown in a previous work [6] the experimental data by H. B. Bell, J. B. Murad and P. T. Carter [7] agree well with the theoretical values calculated from the above equation.

H. Flood et al. have demonstrated by calculation of more complex equilibria that good results are obtained even though the activity coefficients are assumed to cancel one another. This is, for example, the case for the distribution equilibrium of phosphorus in steelmaking.

It should also be mentioned that in reciprocal salt reactions with ΔG_{ex}^0 different from zero, as in our previous equation:

$$\frac{\gamma_{\text{NaBr}} \gamma_{\text{KCl}}}{\gamma_{\text{NaCl}} \gamma_{\text{KBr}}} = \exp \left(\frac{\Delta G_{\text{ex}}^0}{RT} \right) \quad (23)$$

where the activity coefficients must differ from unity, we can get a good approximation formula by assuming regular solution:

$$\ln \gamma_{\text{NaCl}} = N_{\text{K}} N_{\text{Cl}} b_{\text{NaCl}}. \quad (24)$$

By combining the equations (23) and (24), we find that:

$$b_{\text{NaCl}} = \frac{\Delta G_{\text{ex}}^0}{RT}. \quad (25)$$

Flood et al. have previously derived this formula by introducing some approximations when solving the four thermodynamic equations for the activity coefficients in a reciprocal salt melt. A great advantage of this simplified treatment is that it can easily be extended to multicomponent systems by introducing additional terms for every reciprocal equilibrium that can be set up. The generalized formula can be written:

$$RT \ln \gamma_{\text{M}_i\text{A}_i} = \sum_{\substack{j=1 \\ j \neq i}}^r N'_{\text{M}_i(+)} \cdot N'_{\text{A}_j(-)} \cdot \Delta G_{\text{M}_i\text{A}_j}^0. \quad (26)$$

We have an example of the applicability of this formula in H. Flood et al.'s [8] calculations of the FeO activity in complicated slags containing the ions: Fe^{2+} , Ca^{2+} , Mn^{2+} , Mg^{2+} , F^- , O^{2-} , PO_4^{3-} and SiO_4^{4-} . The calculated γ_{FeO} at different concentrations and temperatures shows good agreement with experimentally determined values.

Even though approximate activity calculations are useful when considering a number of practically important metallurgical equilibria, we still have only a limited understanding of the laws involved. However, this is in most cases sufficient, the limits of uncertainty for most of the measured metallurgical equilibria being taken into account. It is to be hoped that future research work in this field will increase the available amount of exact, thermodynamic data for molten salts and slags. Then, possibly, by means of more refined theories, a simple expression of the form:

$$a_{\text{MA}}(\text{in melt}) = \text{function of (concentrations, ionic radii, charges, electron configurations etc. of the ions in the mixture)}$$

for the solution of even more complicated systems, may be derived.

Acknowledgement

Thanks are extended to The Royal Norwegian Council for Scientific and Industrial Research for financial support of this work.

ÚVOD DO KONCEPCIE AKTIVITY A JEJ APLIKÁCIA NA ROZTAVENÉ SOLI A TROSKY

K. Grjotheim, C. Krohn

Ústav anorganickej chémie Nórskej vysokej školy technickej,
Trondheim

Na základe Temkinovej definície aktivity v roztavených soliach sa rozoberá metóda výpočtu termodynamickej aktivity v recipročných sústavách roztavených solí. Metóda je založená na klasických termodynamických predstavách, a to na výmenných reakciách v sústave, na rovnovážnej výmene iónov a na aplikácii Gibbsovej—Duhemovej rovnice.

АКТИВНОСТЬ И ЕЕ ПРИМЕНЕНИЕ В ОБЛАСТИ РАСПЛАВЛЕННЫХ СОЛЕЙ И ШЛАКОВ

К. Гриотгейм, Ц. Крогн

Кафедра неорганической химии Норвежского политехнического института,
Трондгейм

В работе рассматривается возможность расчета термодинамической активности компонентов во взаимных системах расплавленных солей, на основании определения активности по Темкину. Метод базируется на представлениях классической термодинамики, а именно на взаимных реакциях в системе, на равновесном обмене ионов и наконец на применении уравнения Гиббса—Дюгема.

Preložil M. Malinovský

REFERENCES

1. Hildebrand J., *J. Am. Chem. Soc.* **51**, 66 (1929).
2. Temkin H., *Acta Physicochimica* **20**, 411 (1945).
3. Flood H., Førland T., Toguri J. M., *Acta Chem. Scand.* **17**, 1502 (1963).
4. Kleppa O. J., *Report from Symposium on Thermodynamics and Thermochemistry*, p. III : 4 : 1 ff. Lund, Sweden 1963.
5. Flood H., Muan A., *Acta Chem. Scand.* **4**, 364 (1950).
6. Grjotheim K., *J. Metals* **4**, 1173 (1952).
7. Bell H. B., Murad J. B., Carter P. T., *J. Metals* **4**, 7 (1952).
8. Flood H., Førland T., Grjotheim K., *Z. anorg. Chem.* **276**, 289 (1954).

The adress of the authors:

*Prof. Dr. Kai Grjotheim, Dr. Conrad Krohn, Institute of Inorganic Chemistry,
The Technical University of Norway, Trondheim, Norway.*